THE DETERMINATION OF GOLD BY X-RAY FLUORESCENCE ANALYSIS - RADIOISOTOPE EXCITATION AND K-LINE MEASUREMENT (Cost-Shared)

Final Report by: Prof. I.V.Mitchell

Department of Physics

University of Western Ontario

London, Ontario N6A 3K7

Canada

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Dept. E M & R

CANMET/MSL Division

555 Booth St.

Ottawa, Ontario K1A 0G1

Canada

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EXECUTIVE SUMMARY

The purpose of this project was to investigate the possibility of determining the gold content of powdered ore samples, based upon measurement of Au K X-ray intensities excited by photons from the radioisotope ^{133}Ba.

A simple yet flexible system for varying the geometry of source, sample, apertures, absorbers and a Si(Li) X-ray spectrometer was constructed, and a 370 MBq (10 mCi) source was purchased and installed. Spectral evidence for Au K X-rays is clearly found for ^{133}Ba excitation at 314 ppm Au concentration in a powdered ore standard, but could not be found for a reference sample containing 21.4 ppm. A detection limit of approximately 150 ppm is derived. We conclude that Au K X-ray fluorescence by ^{133}Ba is not a viable approach to gold assay in matrices similar to those studied.

SOMMAIRE EXECUTIF

Le but de ce projet était d'examiner la possibilité de déterminer le contenu d'or dans des samples de minéraux poudreux, basé sur les intensités de rayons-X K de Au excités par les photons de la radioisotope ^{133}Ba.

Un système incompliqué mais flexible pour varier la géometrie de la source, la sample, les ouvertures, les absorbants, et un spectromètre rayon-X Si(Li) a été construit, et une source 370 MBq (10 mCi) a été achetée et installée. Il y avait de preuve spectrale pour les rayons-X K de Au à une concentration d'or de 314 ppm dans un minéral poudreux étendard, mais il n'y en avait pas pour les samples de référence contenant 21.4 ppm. Alors, une limite de détection de ~ 150 ppm a été dérivée. On conclut que la fluorescence des rayons-X K d'or par ^{133}Ba ne fournit pas de mèthode viable pour l'analyse de l'or dans les matrices semblables à celles examinées.

INTRODUCTION

X-ray fluorescence (XRF) techniques have been applied extensively to impurity analysis in bulk materials, including minerals. The variant on this method, which is to use radioisotope sources to provide the incident photon flux is much less well developed. It was the purpose of this study to determine whether the use of ^{133}Ba showed promise for Au.

The obvious advantages are its long half-life (10.74 y) and the presence in its γ-ray spectrum of a strong line at 81.0 keV energy, i.e. high enough to excite vacancies in the Au K shell, but insufficient in energy to ionize the K shell of lead, a popular choice for shielding material.

The disadvantages are immediately apparent: the same photon that efficiently ionizes the Au K shell produces an intense Compton backscatter peak at ~ 62 keV, i.e. close in energy to the Au Kα X-ray lines at 67 and 69 keV; the presence of a multitude of γ-rays of higher energies up to 384 keV in the ^{133}Ba spectrum give rise to unwanted continuum backgrounds.

Our approach has been to construct a simple X-ray fluorescence system allowing for flexibility in source/sample/detector geometry and to adopt a spectrometer which is relatively transparent to the high energy photons, viz. a Si(Li) rather than a Ge-type detector. In most other respects, the methodology is standard. With the use of reference powdered ore samples containing known amounts of gold, a detection limit may be extracted.

EXPERIMENT

We have used a 370 MBq (= 10 mCi) annular γ-emitting source of ^{133}Ba[1] to create inner shell vacancies in target atoms, viz. to fluoresce Au atoms. Au K X-rays of ~ 68 keV energy are emitted during the subsequent decay. The geometry chosen was of reflection type; suitable absorbers

[1] purchased from Isotope Products Laboratories, Burbank, Calif., USA

were chosen to reduce the intense radiation from the source itself. Specifically, we have used a combination of Pb, Ag, Cu and Al filters to convert the intense higher energy γ's to low energy radiation. Spectra have also been taken using a large volume (~ 206 cm^3) high purity Ge detector in combination with a ~ 330 kBq ^{133}Ba source, in lieu of the Si(Li) detector.

Figure 1 shows a photograph of the detector assembly system, including apertures, absorbers, source, sample, etc. All components were positioned in a cylindrically symmetric fashion along the axis of the Si(Li) detector. The design configuration allowed for variable geometry for each component individually: i.e. the distances *between* components could be altered in a reproducible manner.

The detector itself was a Kevex Li-drifted silicon [Si(Li)] X-ray detector of area 30 mm^2 with a sensitive depth of 3 mm for an applied bias voltage of 900 volts. The detector was fitted with a Be vacuum window of thickness 8 μm. Detector pulses were fed into a Model 2003 Kevex preamplifier with a LN_2 cooled FET, and amplified using a Kevex Model 4525P (pulsed optical feedback) main amplifier. The overall system resolution was 175 eV at 5.9 keV and ~ 0.5 keV at 68 keV. The amplified output pulses were directed to a Canberra 8076 ADC and displayed on a Canberra Series 90 MCA, coupled directly to a PDP-11 computer for data storage. Thus, the spectra could be recalled easily for later analysis.

The samples used were:

(i) a 314 ppm mineral ore sample;

(ii) a 21.4 ppm reference gold ore (CCMET-MA-1a);

(iii) a 1.39 ppm reference gold ore (CCMET-MA-2a).

All of these samples were provided to us by Dr. L. Dalton, CANMET.

OBSERVATIONS

Figure 2 shows a portion of the photon spectrum emitted by the 370 MBq ^{133}Ba source (source-detector distance ~ 2 m, in order to keep the counting rate reasonable). The decay scheme for this isotope is shown in Figure 3, together with the γ-rays emitted and their listed relative intensities, ref.1. The 81 keV line will be the most efficient for fluorescing the Au K shell. The observed intensities reflect, of course, the intrinsic energy-dependent efficiency of the Si detector. This efficiency was determined using a variety of X-ray sources for photon energies exceeding ~ 25 keV, see Figure 4. For the low energy region (0.5 keV < E_x < 14 keV), the intrinsic efficiency can be deduced using a different technique, see reference 2. It is seen that the Si(Li) efficiency is low for photon energies exceeding 100 keV, which accounts for our initial preference for a Si detector over a Ge detector because of its favourable transparency to intense high energy γ-rays emitted by the ^{133}Ba source.

Using the 314 ppm Au ore standard, we obtained the spectrum shown in Figure 5a for a counting interval (i.e. 'true time') of 55164 s. This figure depicts the *best* spectrum obtained for a variety of geometries that were tried in an attempt to optimize the experimental configuration. The identities of the most prominent X-ray lines are given in Table 1. Figure 5b shows the region in the vicinity of Au Kα in more detail, including a fit to the background. The Au Kα_1 yield deduced from these data is 1719 ± 330 counts, with a signal-to-background value of approximately 30:1; the corresponding value for the Au Kα_2 yield is 1454 ± 379, with a signal-to-background of 50:1. Thus, the Kα_2/Kα_1 ratio is 0.84 ± 0.27, to be compared with the expected ratio of 0.585, ref.3. We observe intense Pb K emission due to the fluorescence of Pb shielding material by the high energy (e.g. 276, 302, 356 and 384 keV) γ-rays emitted by the ^{133}Ba source. This draws attention to one of the disadvantages of the use of the

^{133}Ba source. The Au $K_{\beta 1}$ and $K_{\beta 2}$ lines are not visible against the intense continuum arising from these same hard photons.

We have used the 21.4 ppm reference sample in a second XRF exposure, and observed the spectrum shown in Figure 6. Again we have shown only the region in the vicinity of the Au Kα lines. The smooth curve is a background fit performed in the same manner as for the earlier data. The visibility of either of the Au Kα lines is questionable at best. The Rayleigh (elastically scattered) peak at 81 keV is barely visible.

Since there was no convincing evidence for the presence of Au Kα yield from the 21.4 ppm sample, we have chosen to use the 1.39 ppm reference ore as a blank. We have fluoresced this sample to rule out any possibility of a secondary fluorescence contribution from the approximately 200 Å thick Au contact layer on the Si diode itself. In other investigations to study Au K excitation using the XRF technique (e.g. ref. 4-7), no mention of this source for Au K X-rays has been made. Presumably, yield from this source sets the ultimate detection limit for either Si or Ge detectors, since many of the latter are fabricated also with a Au contact layer. The data are shown in Figure 7 for a counting time of 28000 s. The background fit is shown as a smooth curve and, as before, we see no measurable evidence for Au Kα X-rays, which suggests that the Au contact layer is not contributing to the yield for either the 314 ppm or 21.4 ppm samples.

In order to confirm that the measurements made with a ^{133}Ba source and a Si(Li) detector were not inferior to those that would be obtained using a Ge detector, we used a large volume (~ 206 cm^3) HPGe detector and fluoresced Au K X-rays from the same 314 ppm sample as before, also in reflection geometry with the 330 kBq source. After 2400 s, there was no sign of these X-rays and further counting seemed unproductive. It should be noted that in all measurements, the use of stronger radioisotope sources brings no benefit if the spectrometer system is operating at or close to

its maximum countrate. For this Si(Li) spectrometer, the limit is ~ 3000 cps before system resolution begins to deteriorate. The room background in all cases contributed less than 1 % to the total counts in the Au Kα region of interest.

DISCUSSION

From the data obtained using the reference samples, we conclude that a detection limit for Au in similar matrices is ~ 150 ppm, i.e. approximately one half of the concentration observed by XRF shown in Figure 5b.

The detection limit for XRF detection of Au using a ^{133}Ba source in ore mineral samples of the type studied here is limited by two principal factors. First, the Au Kα peaks are situated on a falling 'background' arising from the Compton backscatter peak of the 81 keV γ-ray, which occurs near 61.5 keV. The intensity of this peak is proportional to the atomic number of the scattering medium. If the samples were primarily composed of lower-Z material (e.g. human tissue, see refs. 6 and 7), then the detection limit using this technique might be somewhat lower. Second, in attempting to neutralize the effects of the higher energy γ-rays from this source via the use of a Si detector, we cannot totally eliminate a relatively energy independent Compton continuum in the detector which is responsible for the approximately flat background in the region where Au Kβ X-rays occur. Thus, we are unable to observe evidence of Au Kβ X-rays for even the 314 ppm reference sample.

Dr. I.K. MacKenzie (University of Guelph) has kindly provided us with an X-ray fluorescence spectrum obtained using the 314 ppm Au standard but for a ^{109}Cd source of approximate strength ~ 7 MBq. The decay scheme for this isotope is very simple, as it emits a single photon at 88 keV. That spectrum, obtained with an HPGe detector in reflection geometry (see

ref. 8), is shown in Figure 8 for the X-ray region of interest. Because the backscattering peak occurs near 65 keV for the 88 keV primary photons, the Au Kβ lines provide the cleanest evidence of the Au concentration. This spectrum was obtained with a counting period of approximately 7200 s. Dr. MacKenzie has also examined the 21.4 ppm reference sample for a counting interval of approximately 55000 s, and the corresponding spectrum is shown in Figure 9. The conclusion from these data is that the lower practical limit of detection for Au in similar ore matrices is ~ 20 ppm using this technique, but such long counting times are obviously still unattractive for mineral assays. Additionally, the half life of 453 days for ^{109}Cd is a handicap for field work.

CONCLUSIONS

We conclude that the intrinsic characteristics of the γ-ray emitting isotope ^{133}Ba set a detection limit of ~ 150 ppm Au in the reference ores provided to us.

Published literature on the use of alternative radioisotope sources to fluoresce Au K X-rays for Au determination suggests limits down to perhaps 50 ppm in favourable cases (low atomic number matrices). The unpublished results of the collaborative work from Dr.I.K. MacKenzie are consistent with this view.

We believe that serious thought should be given instead to an Au activation process, where orders of magnitude higher sensitivity (almost background free) may be achieved.

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(4) M.Kasrai, L.Fozoonmayeh and H.Payrovan, X-Ray Spect. 17 (1988) 219.

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(6) J.Bacso, I.Uzonyi and B.Dezso, Appl.Radiat.Isot. 39 (1988) 323.

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(8) I.K.MacKenzie, Can.J.Phys. 67 (1989) 827.

Table 1: Identification of spectral lines observed when fluorescing the 314 ppm gold ore sample using the ^{133}Ba source.

Channel No.	Energy (keV)	Element
39.5	6.40	Fe Kα
43.0	7.1	Fe Kβ
64.5	10.6	Pb $L\alpha_1$
78.0	12.6	Pb Lβ
91.0	14.8	Pb Lγ
136.0	22.0	Ag Kα
155.0	24.9 / 25.2	Ag Kβ / Sn Kα
161.5	26.3	Sb Kα
183.0	29.7	Sb Kβ
190.5	30.9	Cs Kα
196.5	32.0	Ba Kα
215.0	35.0	Cs $K\beta_1$
223.5	35.8	Cs $K\beta_2$
~ 387	~ 61.5	Compton backscatter
412.0	67.0	Au $K\alpha_2$
423.0	68.8	Au $K\alpha_1$
448.0	72.8	Pb $K\alpha_2$
461.0	75.0	Pb $K\alpha_1$
498.0	81.0	^{133}Ba γ
522.0	84.9	Pb $K\beta_1$
537.0	87.3	Pb $K\beta_2$

FIGURE CAPTIONS

Figure 1

Photograph of experimental configuration used for X-ray fluorescence.

Figure 2

Direct spectrum taken for the 370 MBq ^{133}Ba source, incident on the Si(Li) detector.

Figure 3

^{133}Ba decay scheme and list of principal γ-ray energies with relative intensities.

Figure 4

Relative X-ray detection efficiency for the Si(Li) detector used for the XRF experiments. The calibration sources were positioned 15 cm from the face of the detector.

Figure 5

(a) XRF spectrum registered for 314 ppm reference sample with a 370 MBq ^{133}Ba source and a Si(Li) detector; counting time is 55164 s. (b) spectral region of interest showing the Au Kα lines with a fitted background.

Figure 6

Same as Figure 5b for 21.4 ppm reference sample; counting time is 28000 s.

Figure 7

Same as Figure 5b for 1.39 ppm reference sample; counting time is 28000 s.

Figure 8

XRF spectrum registered for 314 ppm reference sample using a 7 MBq ^{109}Cd source and an HPGe detector; counting time is ~ 7000 s. (courtesy of Dr.I.K. MacKenzie)

Figure 9

Same as Figure 8 for 21.4 ppm reference sample; counting time is 55000 s. (courtesy of Dr.I.K. MacKenzie).

Figure 1

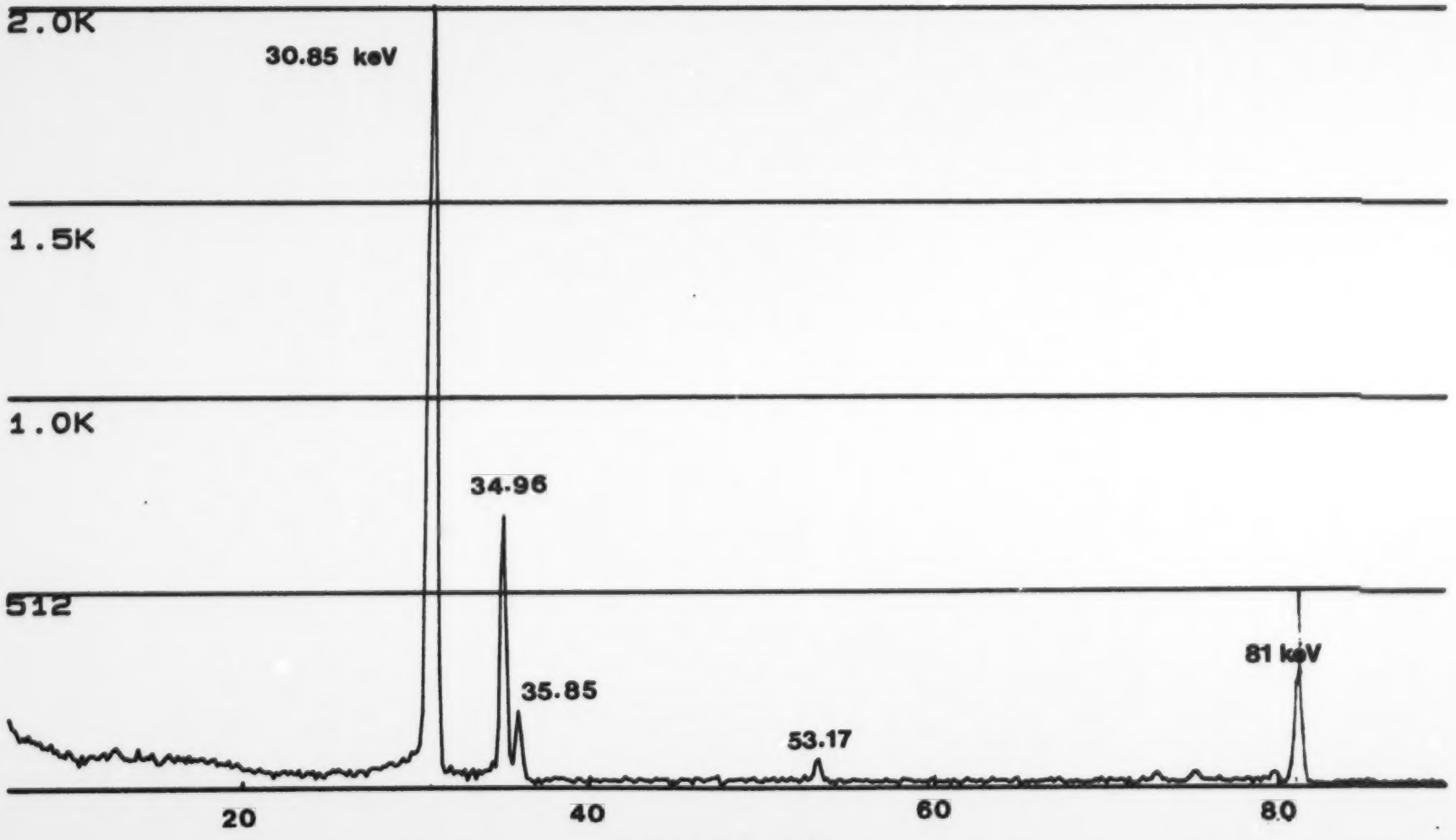
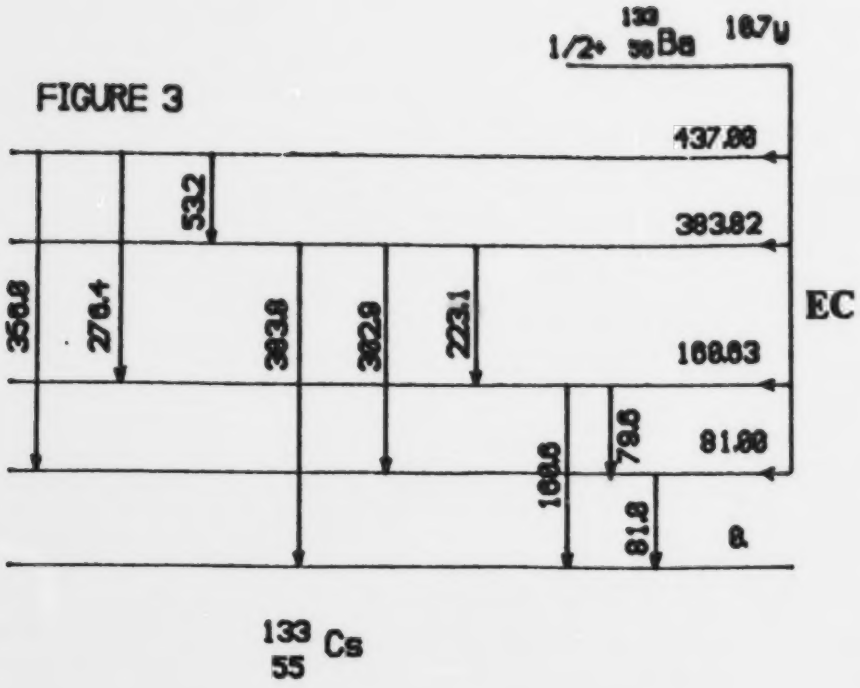

2.0K
30.85 keV
1.5K
1.0K
34.96
512
81 keV
35.85
53.17
20
40
60
80
ENERGY (keV)

FIGURE 2

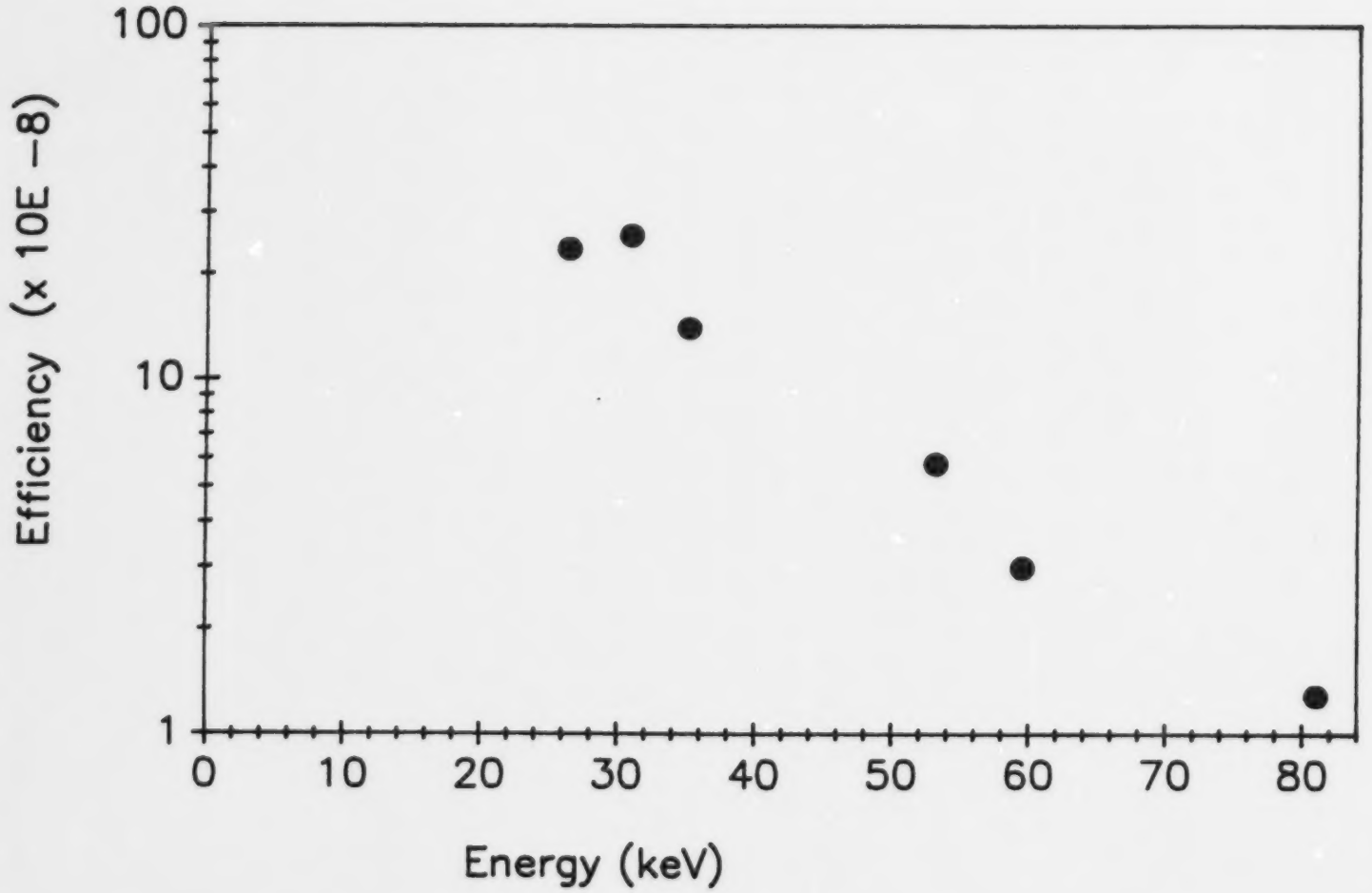
FIGURE 3



LINE	ENERGY	INTENSITY
$Cs_{K\alpha}$ X-ray	30.85	129.0
$Cs_{K\beta}$ X-ray	35.1	33.9
Ba γ-ray	53.17	3.78
"	79.63	4.5
"	81.0	55.3
"	160.63	1.21
"	223.12	0.80
"	276.4	11.43
"	302.9	29.29
"	356.0	100.0
"	383.9	14.47

All intensities are referred to the intensity of the 356 keV line (normalized to 100).

FIGURE 4



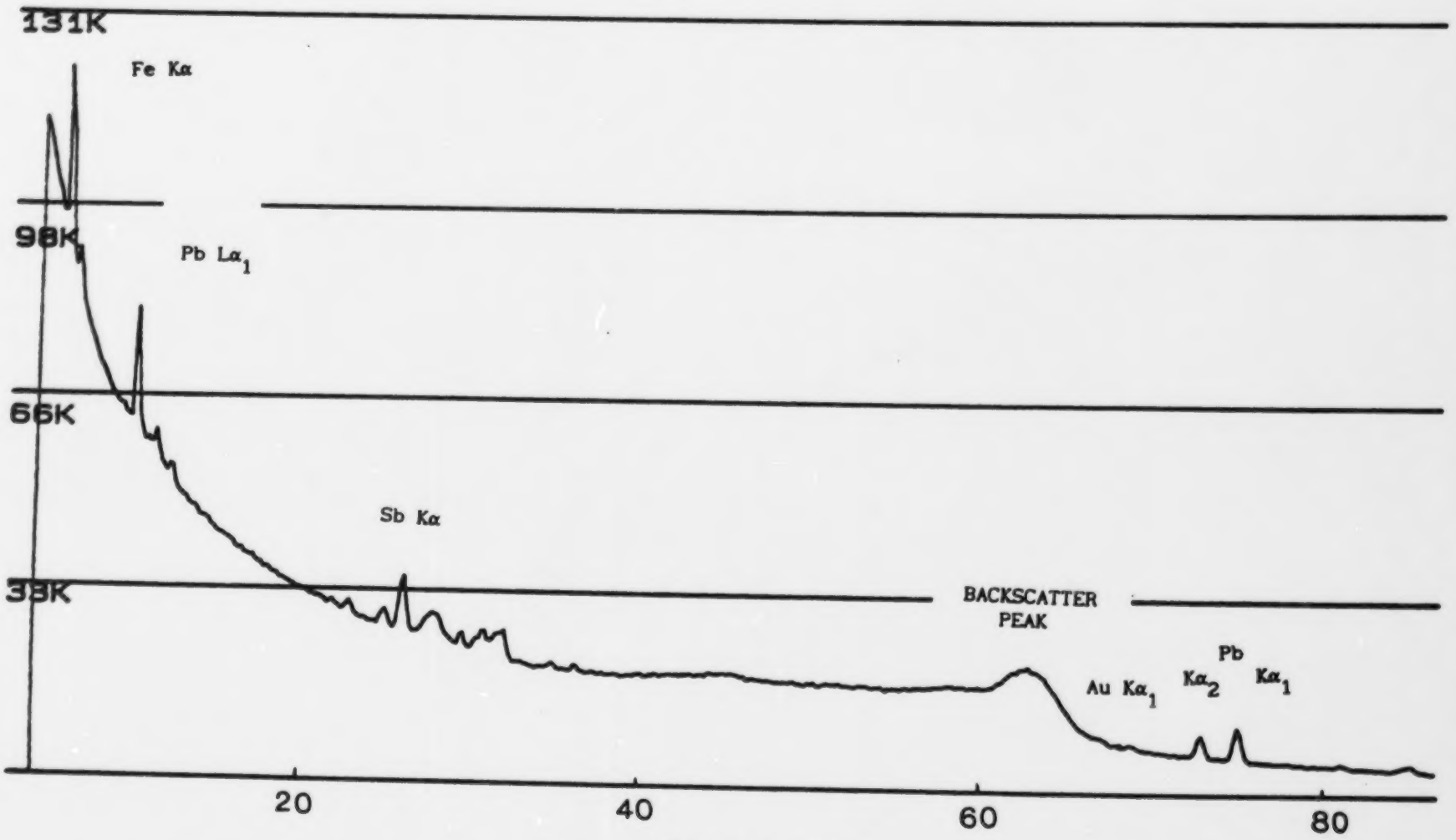

131K
Fe Kα
98K
Pb Lα1
66K
Sb Kα
33K
BACKSCATTER
PEAK
Au Kα1
Pb
Kα2
Kα1
20
40
60
80
ENERGY (keV)

FIGURE 5a

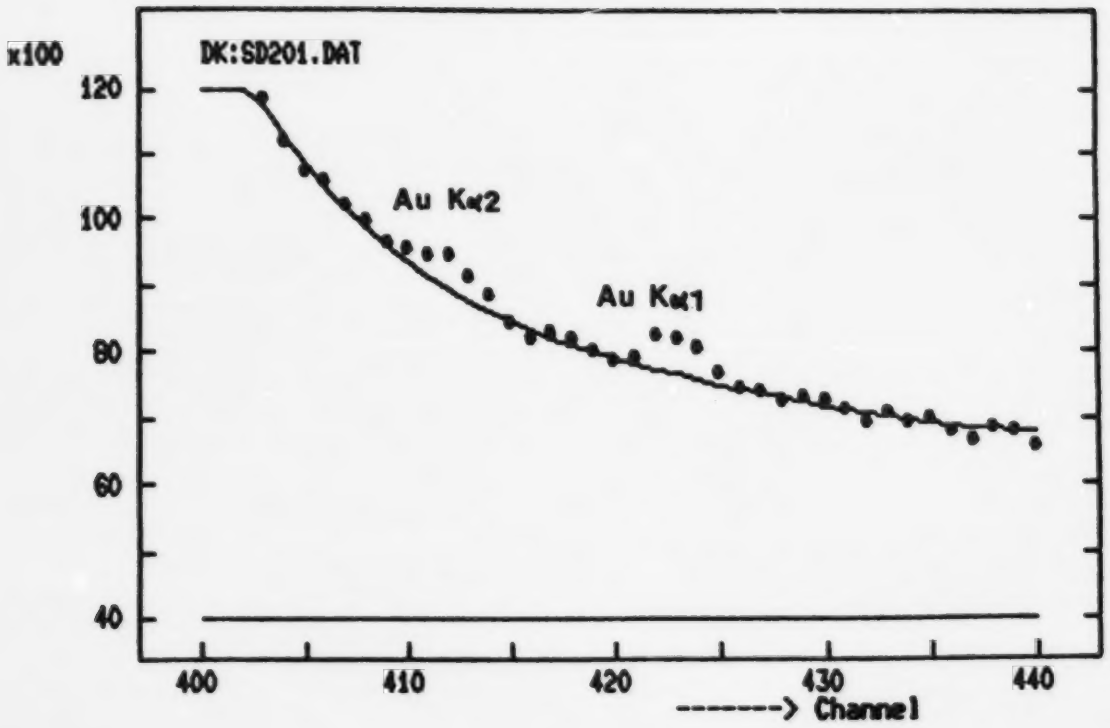

x100
DK:SD201.DAT
120
100
80
60
40
Au Kα2
Au Kα1
400
410
420
430
440
-------> Channel

FIGURE 5b

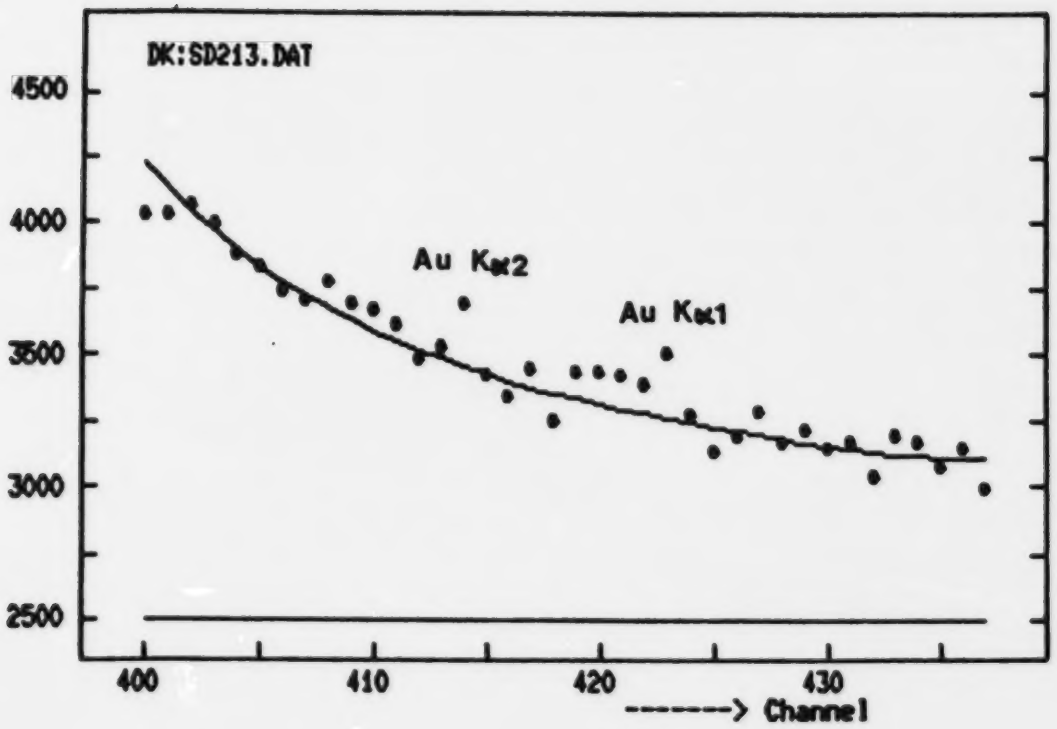

DK:SD213.DAT
4500
4000
3500
3000
2500
Au Kα2
Au Kα1
400
410
420
430
-------> Channel

FIGURE 6

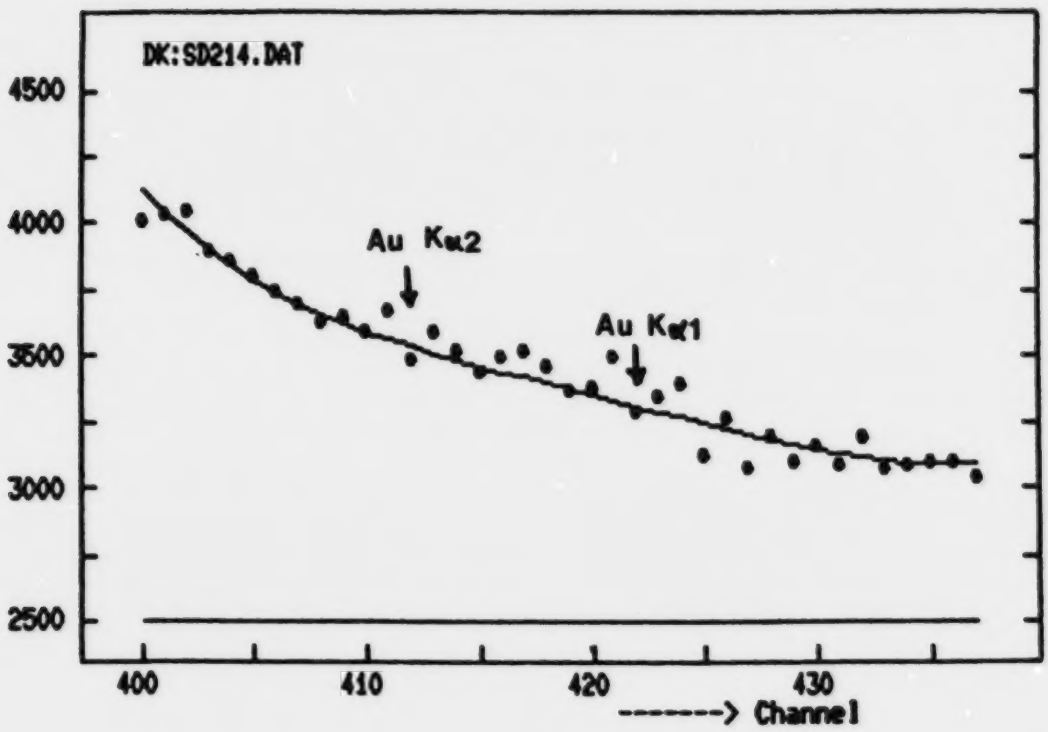

DK:SD214.DAT
4500
4000
3500
3000
2500
Au Kα2
Au Kα1
400
410
420
430
-------> Channel

FIGURE 7

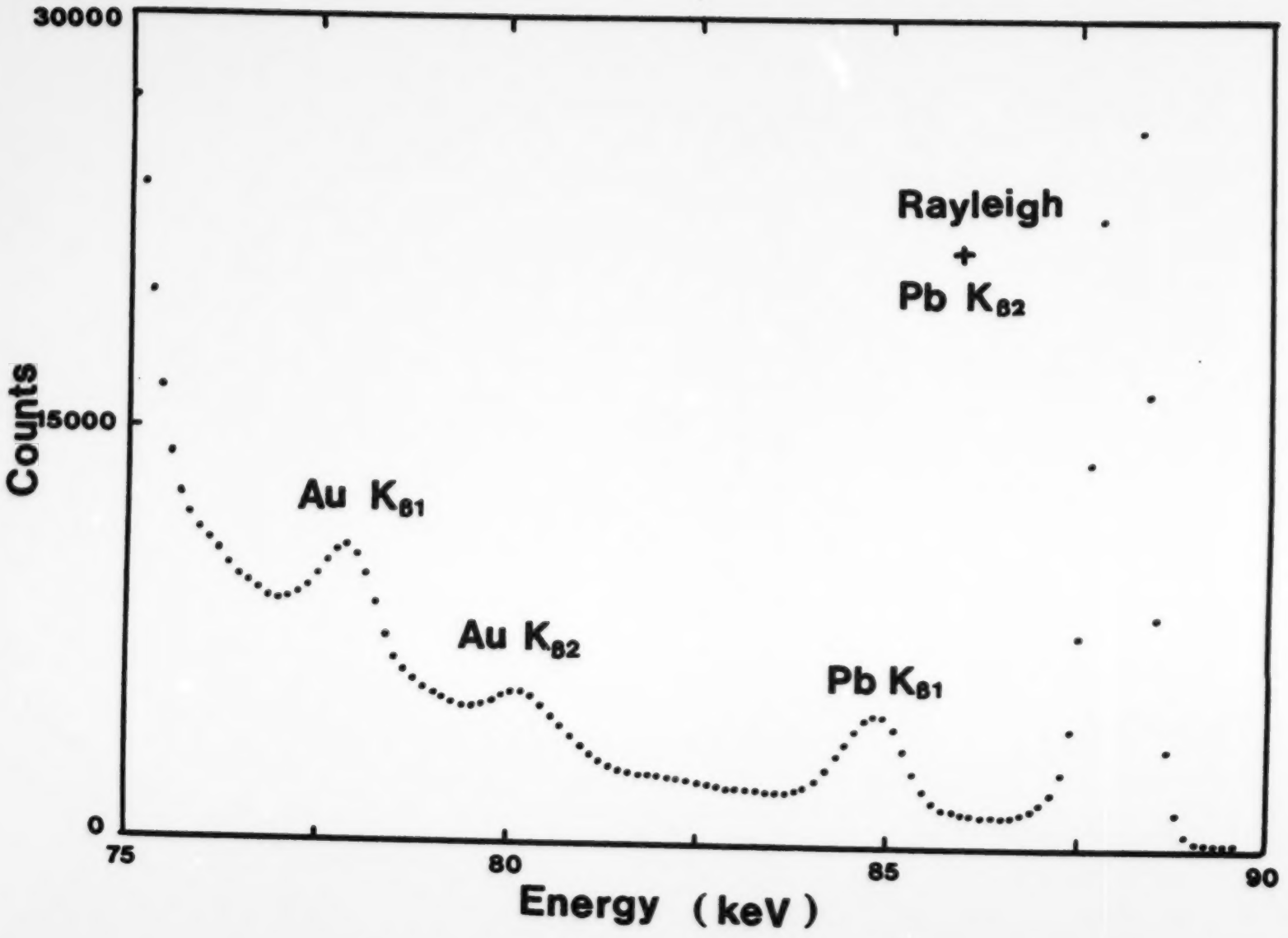

30000
15000
0
Counts
75
80
85
90
Energy (keV)
Rayleigh
+
Pb K$_{\beta 2}$
Au K$_{\beta 1}$
Au K$_{\beta 2}$
Pb K$_{\beta 1}$

FIGURE 8

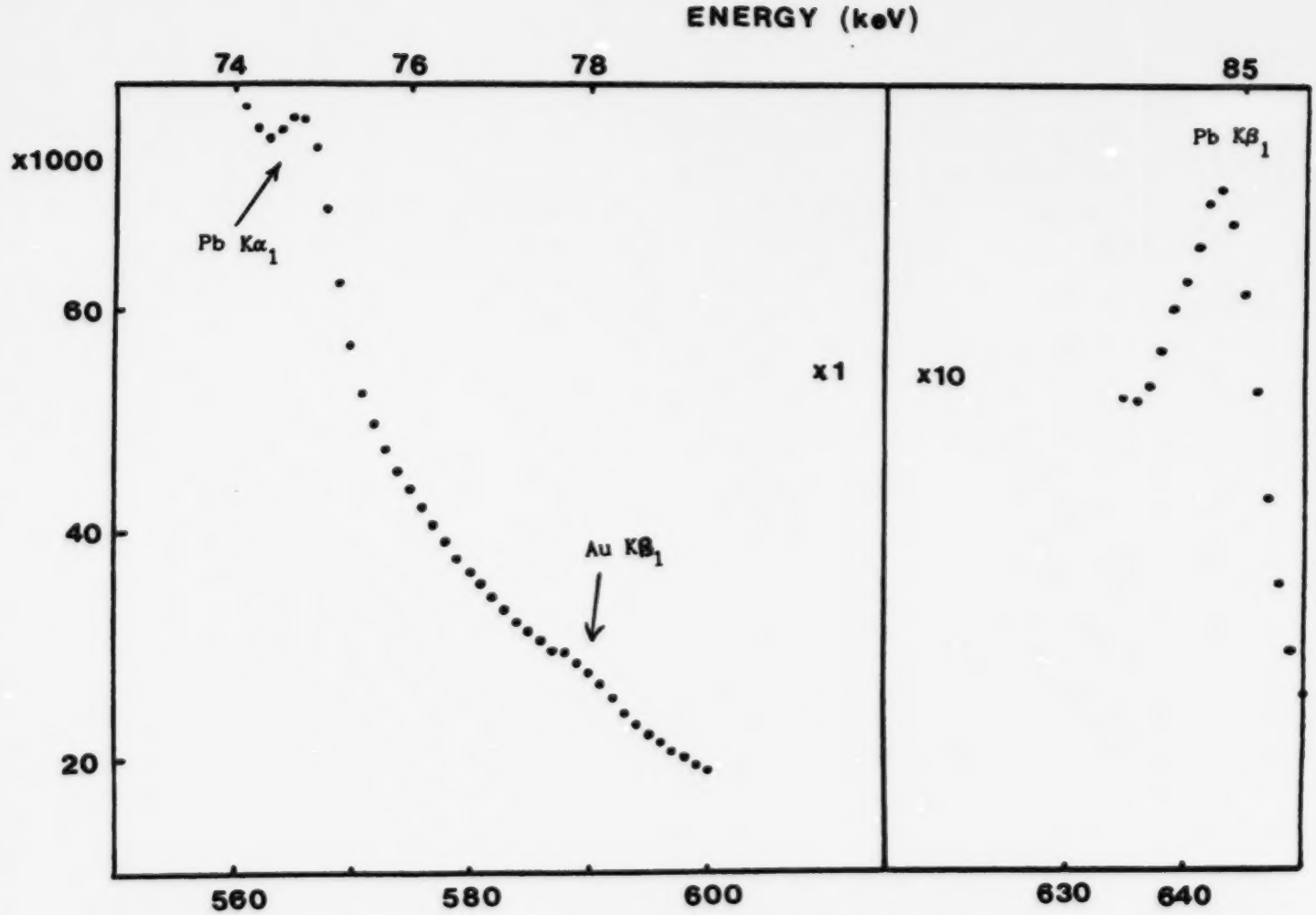

ENERGY (keV)
74
76
78
85
x1000
60
40
20
Pb Kα1
Au Kβ1
Pb Kβ1
x1
x10
560
580
600
630
640
CHANNEL NUMBER

FIGURE 9